



US005245043A

United States Patent [19]

Connell et al.

[11] **Patent Number:** **5,245,043**[45] **Date of Patent:** **Sep. 14, 1993**[54] **DI(HYDROXYPHENYL)-1,2,4-TRIAZOLE MONOMERS**[75] **Inventors:** John W. Connell; Paul M. Hergenrother, both of Yorktown, Va.; Peter Wolf, Frankenthal, Fed. Rep. of Germany[73] **Assignee:** The United States of America as represented by the Administrator of the National Aeronautics and Space Administration, Washington, D.C.[21] **Appl. No.:** 905,708[22] **Filed:** Jun. 29, 1992**Related U.S. Application Data**

[62] Division of Ser. No. 650,336, Jan. 24, 1991, Pat. No. 5,182,356.

[51] **Int. Cl.⁵** C07D 249/08[52] **U.S. Cl.** 548/269.4; 548/267.4; 548/267.8; 548/268.6[58] **Field of Search** 548/267.4, 267.8, 268.6, 548/269.4[56] **References Cited****PUBLICATIONS**

Connell et al, "Chemistry and properties, etc." CA 114:144554d (1991).

Voloshin et al, "Inhibiting action of certain, etc." CA 105:50758k (1986).

Dulova et al, "Study of the complexing of, etc." CA 92:29404v (1980).

Antipina, et al "Light Stabilization of polyolefin, etc." CA 77:76506e (1972).

Primary Examiner—Patricia L. Morris*Attorney, Agent, or Firm*—George F. Helfrich[57] **ABSTRACT**

The di(hydroxyphenyl)-1,2,4-triazole monomers were first synthesized by reacting bis(4-hydroxyphenyl) hydrazide with aniline hydrochloride at 250° C. in the melt and also by reacting 1,3 or 1,4-bis-(4-hydroxyphenyl)-phenylene-dihydrazide with 2 moles of aniline hydrochloride in the melt. Purification of the di(hydroxyphenyl)-1,2,4-triazole monomers was accomplished by recrystallization. Poly(1,2,4-triazoles) (PT) were prepared by the aromatic nucleophilic displacement reaction of di(hydroxyphenyl)-1,2,4-triazole monomers with activated aromatic dihalides or activated aromatic dinitro compounds. The reactions were carried out in polar aprotic solvents such as sulfolane or diphenylsulfone using alkali metal bases such as potassium carbonate at elevated temperatures under nitrogen. This synthetic route has provided high molecular weight PT of new chemical structure, is economically and synthetically more favorable than other routes, and allows for facile chemical structure variation due to the availability of a large variety of activated aromatic dihalides.

3 Claims, No Drawings

DI(HYDROXYPHENYL)-1,2,4-TRIAZOLE MONOMERS

ORIGIN OF THE INVENTION

The invention described herein was jointly made by employees of the United States Government and an employee of BASF A. G., and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

CROSS-REFERENCE

This application is a divisional application of copending patent application Ser. No. 07/650,336 filed Jan. 24, 1991, now U.S. Pat. No. 5,182,356.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to the field of di(hydroxyphenyl) monomers and more particularly to di(hydroxyphenyl)-1,2,4-triazole monomers.

2. Description of the Prior Art

Poly(1,2,4-triazoles) (PT) are heterocyclic polymers which were first synthesized by the reaction of bistetrazole monomers and a bisimidoyl chloride monomer. [C. J. Abshire and C. S. Marvel, *Makromolecular Chemistry*, 44/46,388 (1961)]. Since then several different reaction pathways have been developed to prepare these polymers. The next method of preparing PT involves reacting a polyhydrazide with aniline. This reaction when carried out in polyphosphoric acid at approximately 175° C. produces PT of high molecular weight. [J. R. Holsten and M. R. Lilyquist, *Polymer Science*, A, 3, 3905 (1965)]. Another synthesis of PT involves reacting a bisamidrazone (also referred to as a bishydrazidine) monomer at low temperatures with a diacid chloride monomer. The resulting precursor polymer (poly N-acylamidrazone) is then cyclized either to the poly(1,2,4-triazole) or the poly(1,2,4-oxadiazole), depending on the reaction conditions. The poly(1,2,4-triazoles) prepared by this route have been shown to contain approximately 4% oxadiazole and uncyclized amidrazone along the backbone. [M. Saga and T. Shono, *Jour-*

nal of Polymer Science, B, 4, 869 (1966). Also, V. V. Korshak, "Heat Resistant Polymers" Israeli Translation, Keter Press Jerusalem, 1971, p. 244-248. See also P. M. Hergenrother, *Macromolecules*, 3(1), 10 (1970)]. The last method for preparing PT involves reaction of a dinitrile compound and bisnitrilimine. This route, however, yields only low molecular weight polymer. [J. K. Stille and F. W. Harris, *Journal of Polymer Science*, A-1, 6, 2317 (1968). Also, J. K. Stille and L. D. Gotter, *Journal of Polymer Science*, A-1, 7, 2492 (1969)]. For a general review of PT see "Thermally Stable Polymers" by P. E. Cassidy, Marcel Dekker, Inc. New York, p. 203.

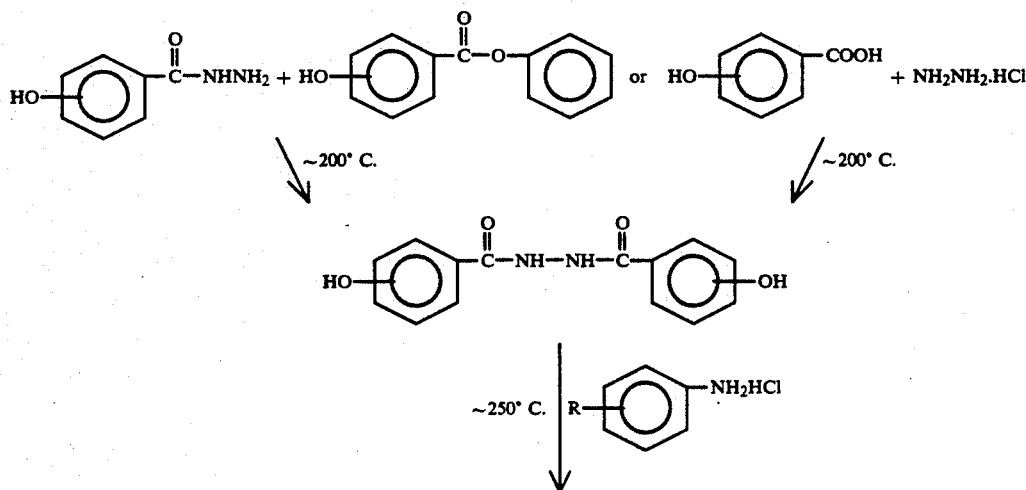
SUMMARY OF THE INVENTION

An object of the present invention is to provide new compositions of several di(hydroxyphenyl)-1,2,4-triazole monomers.

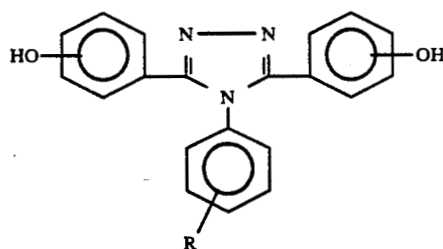
According to the present invention, the foregoing object was obtained by the synthesis of the di(hydroxyphenyl)-1,2,4-triazole monomer as is represented in equation (1). The monomer can be prepared by either of the two routes shown. The chemistry can easily be extended to prepare similar di(hydroxyphenyl)-1,2,4-triazole monomers as shown in equation (2). The aromatic dihydrazides in some cases are commercially available or readily prepared from hydrazine and a di(acid chloride). The substitution of the hydroxy groups in either type of monomer may be meta-meta, para-para, or para-meta. These di(hydroxyphenyl)-1,2,4-triazole monomers are then used to form poly(1,2,4-triazoles) as is shown in equations (3) and (4).

Poly(1,2,4-triazoles) were synthesized by the nucleophilic displacement reaction of di(hydroxyphenyl)-1,2,4-triazole monomers with activated aromatic dihalides. The inherent viscosities (η_{inh}) of the PT ranged from 1.37 to 3.4 dL/g and the glass transition temperatures (T_g) ranged from 192° to 216° C. One polymer exhibited a crystalline melting temperature (T_m) of 377° C. Thermogravimetric analysis (TGA) showed no weight loss occurring below 300° C. in air or nitrogen with a 5% weight loss occurring at approximately 500° C. in air and nitrogen.

EQUATION 1



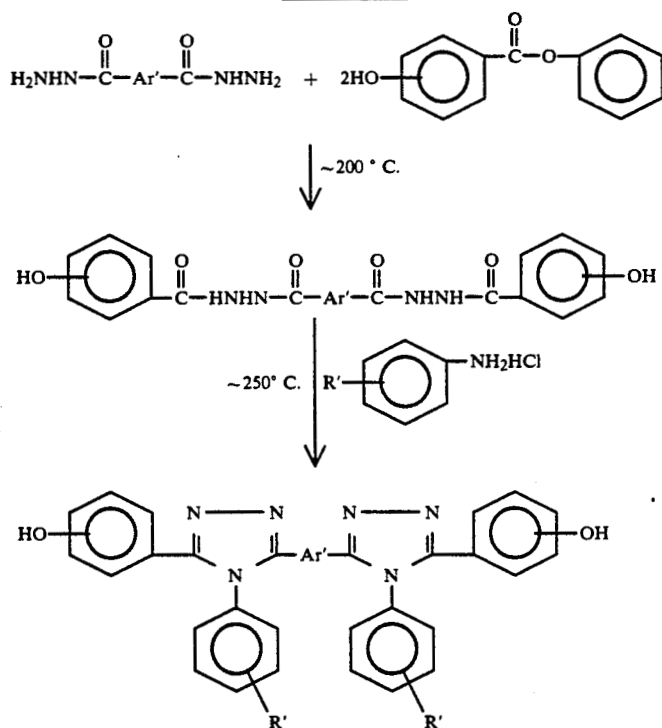
-continued
EQUATION 1



Where R is selected from the group consisting of: H, CH₃, CH₂CH₃, CN, OCH₃, F, Cl, Br, I, phenyl and phenoxy and is either meta or para substituted.

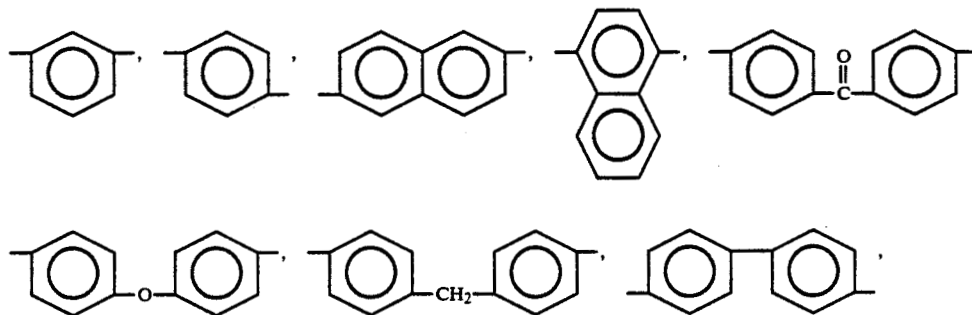
Where R' is selected from the group consisting of: H, CH₃, CH₂CH₃, CN, OCH₃, F, Cl, Br, I, phenyl and phenoxy; and the substitution of R' is either meta-meta,

EQUATION 2

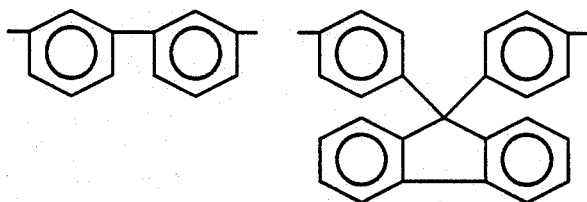
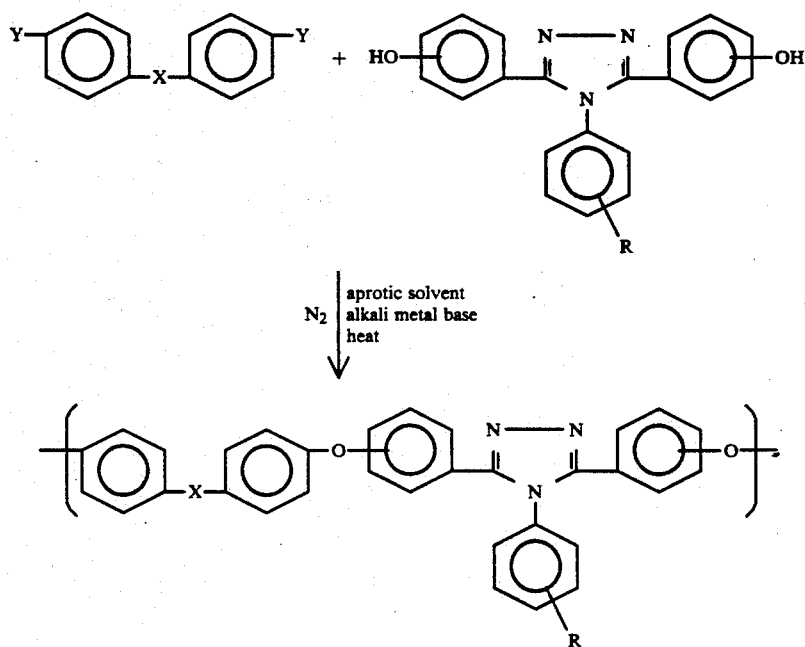
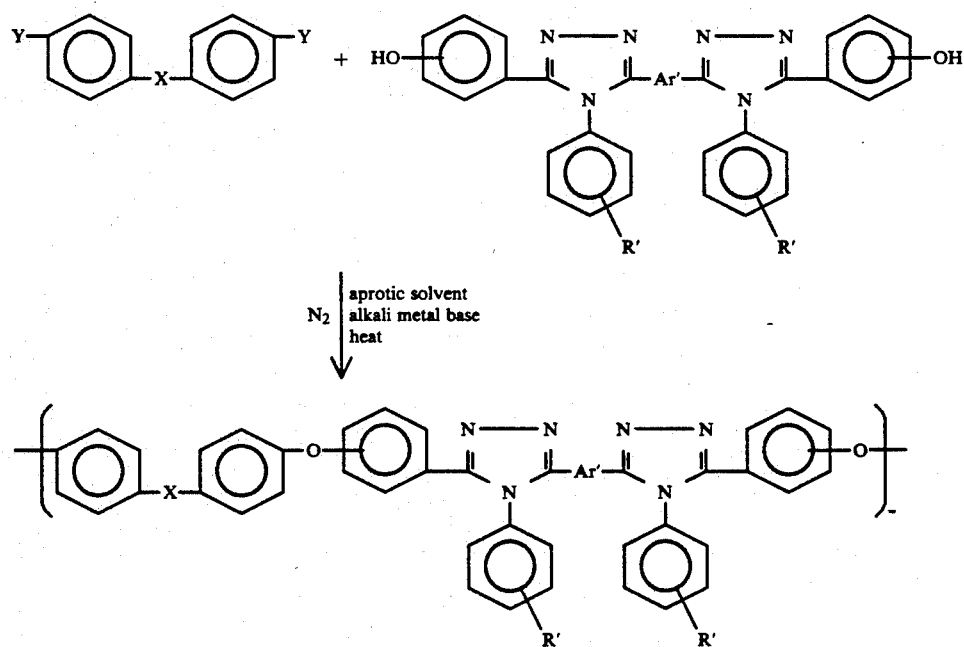


para-para, or para-meta.

Ar' is selected from the group consisting of:



-continued

EQUATION 3EQUATION 4

8

-continued

The figure displays four chemical structures of poly(arylene ether)s, labeled (a) through (d). Each structure consists of two benzene rings connected by a central linkage, with carbonyl groups (C=O) at the 1 and 4 positions of each ring, indicating they are part of a polymer chain.

- (a) Poly(4,4'-oxydiphenylene): The two benzene rings are connected by an ether linkage (-O-).
- (b) Poly(4,4'-methylenediphenylene): The two benzene rings are connected by a methylene linkage (-CH₂-).
- (c) Poly(4,4'-methylenediphenylene sulfone): The two benzene rings are connected by a methylene linkage (-CH₂-), and each ring has a sulfone group (-SO₂-) at the 1 and 4 positions.
- (d) Poly(4,4'-oxydiphenylene sulfone): The two benzene rings are connected by an ether linkage (-O-), and each ring has a sulfone group (-SO₂-) at the 1 and 4 positions.

15

These monomers were then used to prepare poly(1,2,4-triazoles) via an aromatic nucleophilic displacement reaction with activated aromatic dihalides or activated aromatic dinitro compounds. The general reaction sequence is represented by equation (5).

$$\begin{array}{c}
 \text{Y}-\text{C}_6\text{H}_4-\text{X}-\text{C}_6\text{H}_4-\text{Y} + \text{HO}-\text{C}_6\text{H}_4-\text{Ar}-\text{C}_6\text{H}_4-\text{OH} \\
 \downarrow \begin{array}{l} \text{N}_2 \quad \text{aprotic solvent} \\ \text{alkali metal base} \\ \text{heat} \end{array} \\
 \left[\text{C}_6\text{H}_4-\text{X}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{Ar}-\text{C}_6\text{H}_4-\text{O} \right]_n
 \end{array}$$

45

$\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--}, \text{--}\text{SO}_2\text{--}, \text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--}\text{C}_6\text{H}_4\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--},$
 $\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--}\text{C}_6\text{H}_3\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--}, \text{--}\overset{\text{O}}{\parallel}{\text{P}}\text{--}\text{C}_6\text{H}_4\text{--}, \text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--}\text{C}_{10}\text{H}_6\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--},$
 $\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--}\text{C}_{12}\text{H}_8\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--},$
 $\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--}\text{C}_6\text{H}_4\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--}\text{C}_6\text{H}_4\text{--}\overset{\text{O}}{\parallel}{\text{C}}\text{--},$

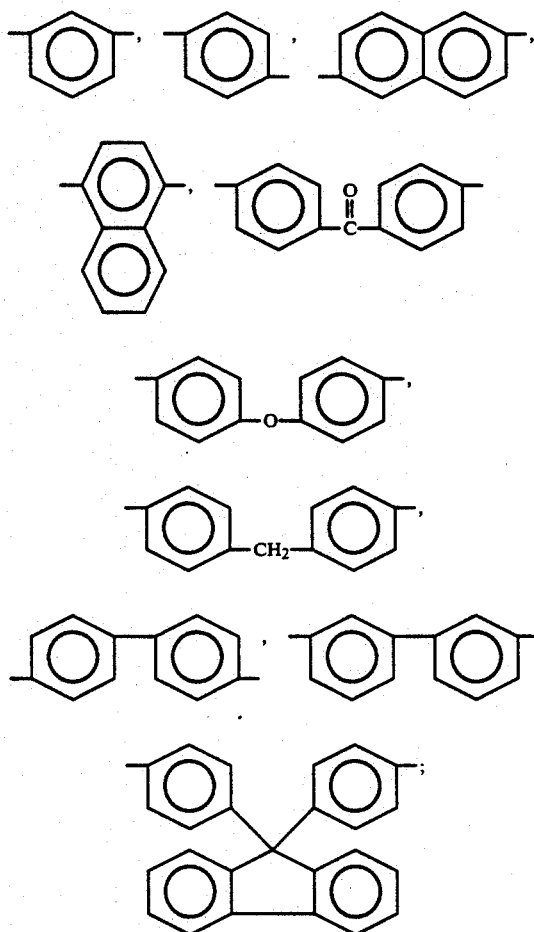
50

55

60

65

wherein Ar' is selected from the group consisting of:



wherein R and R' are selected from the group consisting of: H, CH₃, CH₂CH₃, CN, OCH₃, F, Cl, Br, I, phenyl, and phenoxy; and wherein n is an integer between 4 and 100. The R groups may be substituted either meta or para and the R' groups may be substituted either meta-meta, para-para, or para-meta. Likewise, the hydroxy groups may be substituted either meta-meta, para-para, or para-meta. The reaction was carried out in a polar aprotic solvent such as N,N-dimethylacetamide, N-methylpyrrolidinone, sulfolane, diphenylsulfone, N-cyclohexylpyrrolidinone, dimethylsulfoxide, or mixtures thereof using an alkali metal base such as K₂CO₃, Na₂CO₃, KOH and NaOH. The reaction was then carried out with the application of heat under nitrogen.

Having generally described the invention, a more complete understanding thereof may be obtained by reference to the following examples, which are provided herein for purposes of illustration only and do not limit the invention.

EXAMPLES

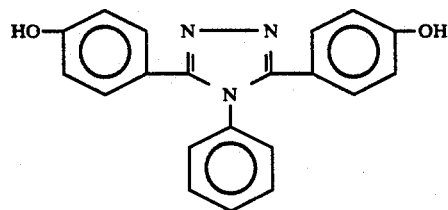
Example I

The following example illustrates the reaction sequence shown in equation (1) above for the preparation of the monomer and the reaction shown in equation (3) above for the preparation of the polymer where X is equal to a carbonyl group and Y is F.

Monomer Synthesis

3,5-Bis(4-hydroxyphenyl)-4-phenyl-1,2,4-triazole

Into a 500 ml three neck round bottom flask equipped with a magnetic stirbar, nitrogen inlet, glass stopper, and distillation head was placed 4-hydroxybenzoic hydrazide (60.9 g, 0.4 mol) and phenyl-4-hydroxybenzoate (85.7 g, 0.4 mol). The mixture was heated to approximately 220° C. by use of a Wood's metal bath. The solids melt and phenol began to evolve and was removed via the distillation head. After two hours, aniline hydrochloride (103.6 g, 0.8 mol) was added and the temperature was increased to 250° C. and held for two hours. The mixture was cooled and washed repeatedly in methanol to give a white solid (65.8 g, 50% yield). The solid was recrystallized from N,N-dimethylacetamide (approximately 225 ml) to give, after drying at 200° C. under vacuum, white needles (49.7 g, 37% yield) with a melting point of approximately 420° C. by differential thermal analysis (DTA). Elemental analysis for C₂₀H₁₅N₃O₂: Calculated: C, 72.93%; H, 4.59%; N, 12.76%; O, 9.72%. Found: C, 72.97%; H, 4.63%; N, 12.84%. This monomer has the following structure:



Poly(1,2,4-triazole) Synthesis

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, N₂ inlet, and reflux condenser was placed 3,5-bis(4-hydroxyphenyl)-4-phenyl-1,2,4-triazole (3.0000 g, 9.1 mmol), diphenylsulfone (25 g, 16% solids), and pulverized anhydrous potassium carbonate (2.77 g, 19.9 mmol, approximately 15% excess). The mixture was heated to approximately 180° C. under nitrogen. After 30 minutes at this temperature, 4,4'-difluorobenzophenone (1.9875 g, 9.1 mmol) was added. The temperature was increased to 280° C. and held for one hour, then increased to 300° C. for 30 minutes and 310° C. for an additional 30 minutes. The mixture was cooled to 200° C. and diluted with N-methylpyrrolidinone (NMP, 20 ml) and precipitated into methanol/acetic acid mixture in a high speed blender. The polymer was collected, washed successively with hot methanol, hot water, and hot methanol and dried at 125° C. for 16 hours in a forced air oven. White polymer (4.47 g, 97% yield) with a glass transition temperature of 207° C. was obtained. The inherent viscosity of a 0.5% solution in m-cresol at 25° C. was 2.94 dL/g. Thin films cast from m-cresol gave tensile strength, tensile modulus, and elongation at 25° C. of 13.2 Ksi, 390.0 Ksi, and 8% and at 150° C. of 8.0 Ksi, 277.0 Ksi and 9.2%, respectively.

EXAMPLE II

The following example illustrates the reaction sequence for the preparation of the poly(1,2,4-triazole) as shown in equation (3) above where X equals an isophthaloyl group and Y equals F.

Poly(1,2,4-triazole) Synthesis

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, N₂ inlet, and reflux condenser was placed 3,5-bis(4-hydroxyphenyl)-4-phenyl-1,2,4-triazole (3.2935 g, 10.0 mmol), diphenyl-sulfone (26 g, 19% solids) and pulverized anhydrous potassium carbonate (3.17 g, 22.9 mmol, 15% excess). The mixture was heated to approximately 180° C. under nitrogen. After 30 minutes at this temperature, 1,3-bis(4-fluorobenzoyl)benzene (3.2223 g, 10.0 mmol) was added. The reaction mixture was heated to 280° C. and held for one hour, increased to 300° C. for 30 minutes, and subsequently heated to 310° C. for an additional 30 minutes. The mixture was cooled to approximately 200° C., diluted with NMP (20 ml) and precipitated into methanol/acetic acid mixture in a high speed blender. The polymer was collected, washed successively with hot methanol, hot water, and hot methanol and dried at 125° C. for 16 hours in a forced air oven. White polymer (5.7 g, 93% yield) with a glass transition temperature of 192° C. was obtained. The inherent viscosity of a 0.5% solution in chloroform at 25° C. was 1.37 dL/g. Thin films cast from chloroform gave tensile strength, tensile modulus, and elongation at 25° C. of 13.3 Ksi, 395.6 Ksi, and 6.5% and at 150° C. of 6.7 Ksi, 345.5 Ksi and 5.4%, respectively.

Polymer characterization data and thin film properties of several polymers are set forth in the following Tables 1 and 2, respectively.

TABLE 1

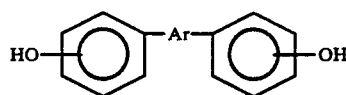
POLYMER CHARACTERIZATION				
POLYMER	X	η_{inh} , dL/g	T _g , °C.	T _m , °C.
P1		2.94	207	—
P2		3.40	216	377
P3		1.37	192	—

TABLE 2

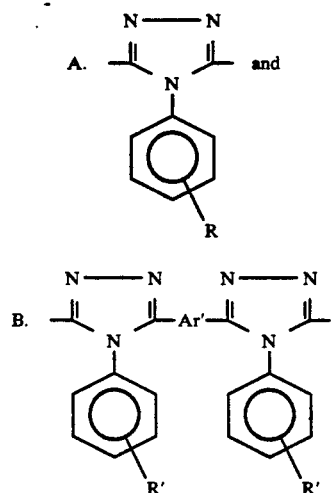
THIN FILM PROPERTIES				
POLYMER	TEST TEMP., °C.	TENSILE STRENGTH, KSI	TENSILE MODULUS, KSI	ELONG., %
P1	23	13.2	390.0	8.1
	150	8.0	277.1	9.2
P2	23	12.7	395.2	7.8
	150	8.0	275.6	9.5
P3	23	13.3	395.6	6.5
	150	6.7	345.5	5.4

What is claimed is:

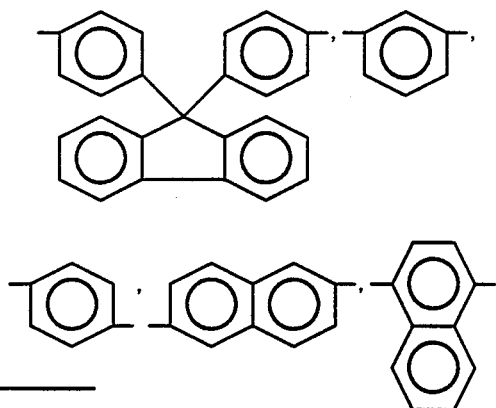
1. A di(hydroxyphenyl)-1,2,4-triazole having the structure



wherein the substitution of the hydroxy radical is selected from the group consisting of: meta-meta, para-para, and para-meta; wherein Ar is selected from the group consisting of:

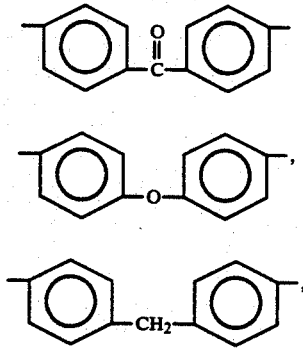


wherein R and R' are selected from the group consisting of: H, CH₃, CH₂CH₃, CN, OCH₃, F, Cl, Br, I, phenyl, and phenoxy; wherein the substitution of R is selected from the group consisting of: meta and para; wherein the substitution of R' is selected from the group consisting of: meta-meta, para-para, and para-meta; and wherein Ar' is selected from the group consisting of:



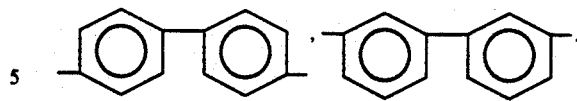
13

-continued



14

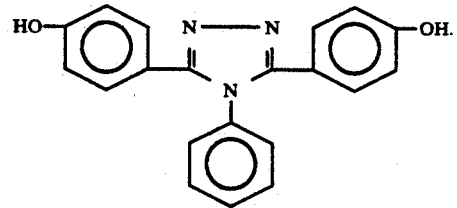
-continued



2. The di(hydroxyphenyl)-1,2,4-triazole of claim 1, having the following structural formula:

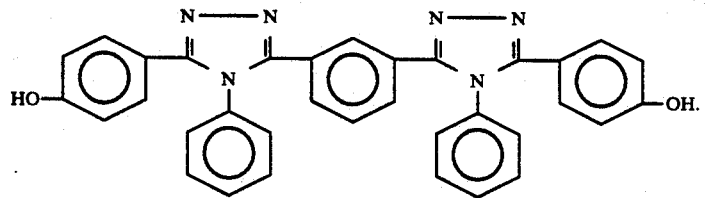
10

15



20

3. The di(hydroxyphenyl)-1,2,4-triazole, having the following structural formula:



* * * * *

35

40

45

50

55

60

65